2,5-cycloaddition products, as earlier reported for $[Os(NH_3)_5(\eta^2\text{-pyrrole})]^{2+}$.[1c] A full report of electrophilic substitution and dipolar cycloaddition reactivity for η^2-pyrrole and substituted pyrrole complexes is forthcoming.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (PRF 23361-G), to the University of Virginia, and to the University of Richmond (W.H.M.) for support of this research.

Supplementary Material Available: Tables of experimental details, atomic positional parameters, thermal parameters, and bond distances and angles and an ORTEP drawing of the asymmetric part of the unit cell for **1a** (15 pages); table of observed and calculated structure factors for **1a** (75 pages). Ordering information is given on any current masthead page.

Synthesis and Structural-Bonding Analysis of the $[Au_6Ni_{12}(CO)_{24}]^{2-}$ Dianion Containing an Unprecedented 18-Vertex Cubic T_d Metal Core Composed of Five Face-Fused Octahedra: The First Example of a Discrete Gold/Nickel Bimetallic-Bonded Species

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Continuing efforts in our laboratory[1] have been directed toward the syntheses of new high-nuclearity nickel carbonyl clusters through reactions of various transition-metal and main-group compounds with the $[Ni_6(CO)_{12}]^{2-}$ dianion.[2] Here we report the synthesis and structural determination of the novel $[Au_6Ni_{12}(CO)_{24}]^{2-}$ dianion (**1**). This cluster, which represents the first example of a molecular gold/nickel bimetallic-bonded species, possesses a heretofore unknown 18-vertex T_d polyhedron composed of five face-fused metal octahedra.

The Au_6Ni_{12} cluster (**1**) was obtained from a 2:3 molar reaction of $[PPh_3Me]^+{}_2[Ni_6(CO)_{12}]^{2-}$ (0.50 g, 0.40 mmol) and Ph_3PAuCl (0.30 g, 0.60 mmol) in THF at ambient temperature for 18 h under a N_2 atmosphere. After removal of a brown precipitate by filtration, the THF solution was reduced under vacuum to a volume of 15 mL and chromatographed on a SiO_2 gel column. **1** was isolated in ca. 5% yield as the third band eluted from the column. This red, air-unstable cluster, which was crystallized as the $[PPh_3Me]^+$ salt by slow diffusion of diisopropyl ether into a concentrated THF solution, was characterized by infrared and electrochemical measurements and by a single-crystal X-ray diffraction analysis.[3]

The idealized T_d configuration of the $[Au_6Ni_{12}(CO)_{24}]^{2-}$ dianion (**1**) can be formally considered to arise from the condensation of four $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragments in antiprismatic orientations on four alternate faces of a central Au_6 octahedron. Alternatively, the Au_6Ni_{12} core can be described as a composite of four vertex-sharing Au_3Ni_3 octahedra (Figure 1). Each equilateral nickel triangle retains the architecture of the three terminal carbonyl and three doubly bridging carbonyl ligands found in the two $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ moieties comprising the trigonal-antiprismatic $[Ni_6(CO)_{12}]^{2-}$ precursor. Electron counting in this face-fused polyoctahedral cluster, which may be considered to possess globally delocalized metal-metal bonding, gives a total of 236 electrons, which agrees with the predicted cluster valence electron count for four octahedra sharing six vertices (i.e., 4 × 86 − 6 × 18 = 236 electrons).[4,5] The 12 independent, Au-Au distances in the central Au_6 octahedron vary from 2.786 (2) to 2.882 (2) Å; the mean value of 2.835 Å is shorter than the corresponding mean Au-Au distance of 2.98 Å on the "surfaces" of the $Au_{11}X_3(PAr_3)_7$ clusters (where X = I, SCN)[6] but comparable to the mean Au-Au distance of 2.81 Å on the "surface" of the $[Au_9(P\{p\text{-tol}\}_3)_8]^{3+}$ cluster.[7] To our knowledge, there are no previous examples of a noncentered Au_6 octahedron. The yellow $[Au_6(P\{p\text{-tol}\}_3)_6]^{2+}$ dication (where *p*-tol denotes 4-methylphenyl), originally formulated[8] as a noncentered octahedral cluster, was recently shown by Schmidbaur and co-workers[9] to be the $[Au_6(P\{p\text{-tol}\}_3)_6(\mu_6\text{-}C)]^{2+}$ dication with octahedral coordination of the $AuPPh_3$ fragments around an interstitial carbon atom; thus, the carbide-centered atom in this cluster results in a normal electron count[10] and accounts for the unusually long Au-Au distances of 3.02 Å (average).[11-17] In

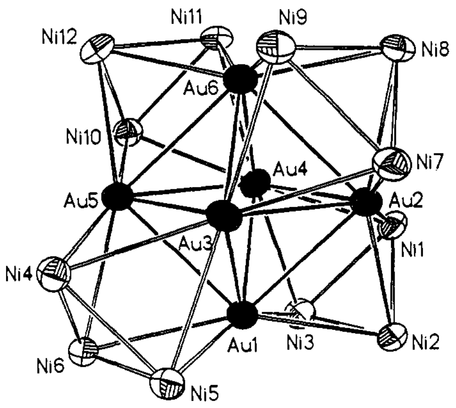

Figure 1. Au_6Ni_{12} core of the 236-electron $[Au_6Ni_{12}(CO)_{24}]^{2-}$ dianion (**1**). This 18-vertex polyhedron of cubic $T_d\text{-}\bar{4}3m$ symmetry may be viewed as a face-to-face condensation of four octahedral Au_3Ni_3 fragments at alternate faces of a central Au_6 octahedron.

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[3] $[PPh_3Me]^+{}_2[Au_6Ni_{12}(CO)_{24}]^{2-}\cdot C_4H_8O$: orthorhombic, *Pbca*, a = 17.730 (5) Å, b = 29.518 (6) Å, c = 30.676 (14) Å, V = 16054 (9) Å^3, Z = 8. The crystal structure (with the independent unit consisting of one dianion, two monocations, and one THF molecule) was determined by direct methods (SHELXTL) followed by successive Fourier and difference syntheses. Anisotropic least-squares refinement converged at $R_1(F)$ = 8.38%, $R_2(F)$ = 7.74% for 7657 independent absorption-corrected reflections ($|F| > 3.0\sigma(F)$) obtained at room temperature via a Siemens (Nicolet) P3/F diffractometer with Mo Kα radiation.

[4] Application of the topological electron-counting (TEC) model[5] to **1** also gives a total valence cluster electron count (N) of 236, as calculated from the equation $N = 2(8V - F + 2 + X)$ where V = 18 vertices, F = 32 exposed triangular (metal-metal bonding) faces, and X = 4 (based upon four vertex-sharing octahedra). The fact that this and other electron-counting procedures do *not* predict the correct electron total for five face-fused metal octahedra emphasizes from a bonding viewpoint that **1** is best considered as the composite of four vertex-sharing Au_3Ni_3 octahedra.

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contrast, the 0.2-Å-shorter Au–Au distances in **1** indicate relatively strong direct Au–Au bonding within the noncentered gold octahedron. The 24 independent Au–Ni distances in **1** range from 2.632 (4) and 2.757 (4) Å with a mean value of 2.69 Å. Although no Au–Ni bond distances have been reported previously, comparison with Au–Co and Au–Cu bond distances indicates that the 2.69-Å distance is consistent with strongly bonding Au–Ni interactions. The average distance of 2.40 Å for the 12 intratriangular carbonyl-bridged Ni–Ni distances (of 2.385 (6)–2.410 (5) Å range) in **1** is virtually identical with the intratriangular carbonyl-bridged Ni–Ni distances in the corresponding $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragments contained in the $[Ni_6(CO)_{12}]^{2-}$ dianion (2.38 Å),[2] in the $[Ni_9(CO)_{18}]^{2-}$ dianion (2.39 Å),[18] and in the $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ anions (n = 2–4).[19]

The Au_6Ni_{12} core may be considered as a segregated bimetallic phase, in which the central part (or kernel) of the core is composed of an aggregate of gold atoms with surface coverage by the nickel atoms. Other mixed-metal carbonyl clusters with segregated bimetallic cores include the $[Pd_6Fe_6(CO)_{24}H]^{3-}$ trianion with a trigonal-antiprismatic (octahedral) Pd_6 kernel,[20] the $[Pt_6Ni_{38}(CO)_{52}H_x]^{4-x}$ anions with an octahedral Pt_6 kernel,[21] and the $[Rh_5Ni_6(CO)_{21}H_x]^{3-}$ trianion with a trigonal-bipyramidal Rh_5 kernel.[22] In the case of **1**, the octahedral gold kernel of each Au_6Ni_{12} particle of pseudo cubic T_d symmetry is encapsulated by 12 symmetry-equivalent Ni surface atoms. The geometrical arrangement of the nickel atoms can be described in terms of a T_d-distorted polyhedron of the 3^24^2 cuboctahedron, a semiregular centrosymmetric polyhedron of cubic O_h symmetry with 12 vertices, six square and eight equilateral triangular faces, and 24 edges.[23] The particular cubic T_d distortion giving rise to the 12-vertex nickel polyhedron in **1** involves the compression of 12 edges (to Ni–Ni bonding distances) comprising one set of four alternate triangular faces and concomitant expansion of the 12 edges comprising the other set of four alternate triangular faces. The particle size of this noncentrosymmetric Au_6-centered nickel polyhedron varies from 5.8 Å in diameter between the two centroids of the opposite compressed and elongated triangular faces along each of the four body-diagonal C_3-3 ⟨111⟩ axes to 5.0 Å in diameter between the two centroids of the opposite rectangular faces along each of the three S_4-$\bar{4}$ ⟨100⟩ axes. Furthermore, **1** may be envisioned as a molecular analogue of the "chemisorption-induced aggregation" model proposed for bimetallic clusters of catalytic interest[24] from surface-science studies. This thermodynamic-based model[25] presumes that the normal surface-enrichment composition rule invoked for bimetallic particles (under ultrahigh vacuum), in which the metal component with the lower heat of sublimation (i.e., normally weaker metal–metal interactions) should concentrate at the surface in order to lower the surface tension, can be reversed if an absorbate gas binds much more strongly to the other metal component with the higher heat of sublimation.[26] Thus, for Ni–Au alloys (and in general for other group VIII (8–10) metal–group IB (11) metal alloys) under an inert atmosphere, the surface-science rule predicts that the gold atoms would concentrate at the surface because the group 11 gold has a lower sublimation energy than that of the group 10 nickel. However, the fact that carbon monoxide chemisorbs strongly and selectively to nickel and not to gold results in the expectation that a CO atmosphere would instead lead to an enrichment of nickel atoms at the surface. It is presumed in **1** that the nickel-coordinated carbonyl ligands play such a role.

An infrared spectrum (THF) of the cluster displayed one band at 2040 (s) cm^{-1} in the terminal carbonyl region and two bands at 1860 (s) and 1840 (m) cm^{-1} in the bridging carbonyl region. The appearance of the corresponding carbonyl bands at much lower wavenumbers (viz., 1975 (s), 1810 (m), and 1780 (ms) cm^{-1}) in a THF spectrum of the $[Ni_6(CO)_{12}]^{2-}$ precursor (as the $[PPh_4]^+$ salt)[2b] suggests a substantial withdrawal of electron density from the carbonyl groups of the four tridentate $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ moieties in **1** by the electron-deficient octahedral gold kernel.

A cyclic voltammogram of the Au_6Ni_{12} cluster exhibited a quasi-reversible reduction at −1.5 V and an irreversible oxidation at 1.4 V, indicative of the resistance of **1** to deviation from the theoretically predicted closed-shell electron count.

Typically, reactions between Ph_3PAuX and anionic transition metal clusters lead to clusters in which the $[Ph_3PAu]^+$ moiety occupies edge-bridging or face-bridging sites within the transition-metal cluster, often without appreciable alteration of the basic skeletal geometry. Thus, cleavage of the Ph_3P ligand from each gold atom with concomitant formation of the Au_6Ni_{12} core of **1** is an unexpected, remarkable consequence of this reaction. In addition to the Au_6Ni_{12} cluster, we have also isolated in low yield and have structurally analyzed the chloro analogue of the $Au_{11}(P\{C_6H_4\text{-}p\text{-}Cl\}_3)_7I_3$ cluster.[6] We are continuing to pursue the isolation and characterization of the remaining products of this reaction as well as an investigation of alternative routes for preparing **1** in larger quantity in order to explore its chemical reactivity.

Acknowledgment. We thank the National Science Foundation for their support of this research. One of us (A.J.W.) is grateful to the Graduate School (UW–Madison) for a first-year Graduate Fellowship during September 1989–August 1990. We also are indebted to Dr. Jeffery Zebrowski and Mr. Randy Hayashi

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(14) Theoretical calculations[15,16] have recently been reported on the electronic structures of the $[Au_6(PR_3)_6(\mu_6\text{-}C)]^{2+}$ dication and other carbon-centered gold clusters. Of prime interest is that these calculations revealed attractive tangential interactions between the Au(I) atoms in these polyaurated organogold compounds with Au–Au distances of 2.9–3.0 Å. These results are in harmony with convincing structural–spectroscopic evidence by Schmidbaur and co-workers[17] for the existence of attractive tangential interactions between Au(I) centers in these and other gold compounds.

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(UW-Madison) for their assistance in part of this work and to one referee for helpful comments. We are most pleased to acknowledge the Johnson-Matthey Inc. loan program (West Deptford, NJ) for supplying a sample of auric acid, from which Ph_3PAuCl was prepared.

Supplementary Material Available: Tables for $[PPh_3Me]^+{}_2$-$[Au_6Ni_{12}(CO)_{24}]^{2-}$ listing atomic coordinates, interatomic distances, bond angles, anisotropic displacement coefficients for the non-hydrogen atoms, and fixed positional and isotropic thermal parameters for the hydrogen atoms (13 pages). Ordering information is given on any current masthead page.

Ribonuclease H Activation by Inert Transition-Metal Complexes. Mechanistic Probes for Metallocofactors: Insights on the Metallobiochemistry of Divalent Magnesium Ion

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Our laboratory is studying the metallobiochemistry of the alkali and alkaline-earth metals.[1-4] Divalent magnesium frequently serves as a metal cofactor for enzymes catalyzing phosphoryl transfer reactions and phosphate ester hydrolysis. In this regard, two mechanistic roles are commonly proposed: (1) reduction of the pK_a for bound H_2O to form an activated nucleophile $[Mg(OH)^+]$ and (2) a combined template/Lewis acid catalyst (I and II in Figure 1, respectively).[5,6] These inner-sphere coordination modes have been successfully adopted in the design of coordination complexes for metal-catalyzed hydrolysis of RNA;[7,8] however, the generality of these pathways for enzymatic nuclease activity has not yet been established.[9,10] Herein, we report the use of inert transition-metal complexes as probes of reaction mechanism and show that both of the above coordination states are ineffective for RNase H, a low molecular weight, magnesium-dependent restriction nuclease that cleaves the RNA strand of RNA·DNA hybrids.[11,17] This is the first demonstration of nuclease activation by formation of an outer-sphere complex with an inert metal cofactor and is of added relevance in view of a recent crystallographic analysis of the structurally related HIV RNase H domain.[18]

We have used cobalt(III) hexaammine as a probe for outer-sphere chemistry of Mg^{2+}(aq), based on the following criteria: (1) $Co(NH_3)_6{}^{3+}$ is similar in size to $Mg(H_2O)_6{}^{2+}$; (2) Co^{3+} is inert, and so exchange of the inner-sphere ligands is slow; and (3) $Co(NH_3)_6{}^{3+}$ can form an outer-sphere H-bond network similar to that formed by $Mg(H_2O)_6{}^{2+}$. RNase H was found to be fully active with $Co(NH_3)_6{}^{3+}$ and $Co(en)_3{}^{3+}$ as replacements for $Mg(aq)^{2+}$. Kinetic parameters were determined from the digestion of $([^3H]\text{-}A{\cdot}dT)_{20}$.[12] These are listed in Table I, which compares the reactivity of RNase H with Mg^{2+}(aq), Mn^{2+}(aq), Ca^{2+}(aq), $Co(NH_3)_6{}^{3+}$, and $Co(en)_3{}^{3+}$, as active-site cofactors. By agarose gel electrophoresis, these reactions show varying rates of digestion of the RNA strand of poly(rA)·poly(dT) to give residual ss DNA.[14] Control experiments with each complex ion and substrate mixture alone gave no reaction.

Examination of the catalytic parameters in Table I demonstrates that both $Co(NH_3)_6{}^{3+}$ and $Co(en)_3{}^{3+}$ show significant reactivity as metal cofactors. It is unlikely that the enzyme can effect a facile pathway for nucleophilic substitution of these complexes by the phosphodiester backbone, thereby activating the diester to hydrolysis,[15] and so $Mg(H_2O)_6{}^{2+}$ is presumably the active complex in the native reaction.[16] The metal cation may serve several functions: (1) provision of electrostatic relief between the negatively charged polynucleotide chain and the catalytic carboxylates at the active site (III, Figure 1); (2) assistance in binding the substrate by formation of bridging hydrogen bonds; (3) stabilization of the active structure of the enzyme; (4) promotion of nucleophilic or base catalysis by an outer-sphere mechanism. Neither a Lewis acid complex with the phosphodiester backbone nor an activated nucleophile $[Mg(OH)^+]$ is a viable intermediate. The latter has been suggested by comparison with the 3′–5′ exonucleolytic activity of DNA polymerase I, which possesses two divalent metal ions and four carboxylates at the active site.[9,18] We conclude that hydrolysis of the RNA backbone by RNase H (*Escherichia coli*) does not result from attack by metal-bound nucleophiles to form an inner-sphere metal-stabilized pentacovalent phosphorus intermediate.[11] Direct attack by solvent H_2O (or carboxylate with subsequent hydrolysis) appears most likely. Reaction rates also depend on the ionic radius of the metal cofactor $[V_{max}(Mg^{2+}) > V_{max}(Mn^{2+}) > V_{max}(Ca^{2+})$ and $V_{max}[Co(NH_3)_6{}^{3+}] > V_{max}[Co(en)_3{}^{3+}]$, Table I; where $r(Mg^{2+}) = 0.86$ Å, $r(Mn^{2+}) = 0.97$ Å, $r(Ca^{2+}) = 1.14$ Å].

Recent crystallographic analyses have demonstrated a close structural relationship between *E. coli* RNase H and the HIV RNase H domain.[11,17,18] These are also structurally related to DNase I, a Ca^{2+}-dependent enzyme.[10,17] In contrast to RNase

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(12) $([^3H]\text{-}A{\cdot}dT)_{20}$ was synthesized by the reaction of $[^3H]$-A (24 Ci/mmol) and a $(dA)_{20}$ template (catalyzed by RNA polymerase), according to standard procedures.[13]

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(14) Reactions were run under conditions recommended by the supplier: RNase H (BRL, 0.5 unit), M^{n+} (10 mM), 0.05 A_{260} poly(rA)·poly(dT), incubation (37 °C, 30 min); terminated with 1 μL of gel-running buffer (5% bromphenol blue, 5% xylene cyanole EE, 5% orange G, 60% glycerol) and run on a 0.8% agarose gel in 1 × TBE buffer at 100 V for 45 min.

(15) Ethylenediammine (en) is a chelating ligand, and so the probability of attack by the poor phosphodiester nucleophile is greatly reduced.

(16) It is possible that one of the carboxylates at the catalytic site may bind directly to Mg^{2+}. The Asp10 to Mg^{2+} distance is 2.0 Å,[11,17] although this may be induced by crystal packing forces. However, $Co(NH_3)_6{}^{3+}$ activates RNase H, and so *coordination by the enzyme has no bearing on the catalytic role of the metal ion.*

(17) Katayanagi, K.; Miyagawa, M.; Matsushima, M.; Ishikawa, M.; Kanaya, S.; Ikehara, M.; Matsuzaki, T.; Morikawa, K. *Nature* **1990**, *347*, 306.

(18) Recent X-ray results on the HIV RNase H domain show two divalent cations surrounded by four acidic residues in the active site (Davies, J. F.; Hostomska, Z.; Hostomsky, Z.; Jordan, S. R.; Matthews, D. A. *Science* **1991**, *252*, 88–95).

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